

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : KURARAY CO LTD

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(72)Inventor : TAKAMATSU HIDEO
KONO NAOTAKE

(54) PRODUCTION OF CYCLIZED POLYMER

(57)Abstract:

PURPOSE: To produce a cyclized polymer excellent in abrasion resistance, chemical resistance and adhesiveness, by cyclizing a specified low-MW isoprene polymer to which a maleic anhydride (derivative) has been added.

CONSTITUTION: A modified polymer is obtained by adding 0.3W12mol%, per isoprene monomer unit of polymer, maleic anhydride (derivative) to a low-MW isoprene polymer, cis-1,4-addition content $\leq 70\%$, viscosity-average MW10,000W 150,000, obtained by an anionic polymerization method, carrying out an addition reaction of the mixture by heating in the presence or absence of a solvent or a radical catalyst. Next, this modified polymer is dissolved in a solvent so that the concentration is 5W80% and then cyclized at room temperature to 200° C for 2W10hr in the presence of an organic sulfonic acid, a Friedel-Crafts catalyst, etc., so that the iodine value of the cyclized polymer is 100W300.

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21 Japanese Patent Application No. 56-30686
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72 Inventor Hideo TAKAMATSU
98, Ohta, Hasaki-cho, Kashima-gun,
Ibaraki-ken
72 Inventor Hisatake MINATONO
98, Ohta, Hasaki-cho, Kashima-gun,
Ibaraki-ken
71 Applicant KURARAY CO., LTD.
1621, Sakazu, Kurashiki, Okayama
74 Representative Ken HONDA (Patent Attorney)

Description

1. Title of the Invention

Process for preparing cyclized polymer

2. Claims

A process for preparing cyclized polymer, wherein a modified polymer produced by adding maleic anhydride or its derivative to a low molecular weight isoprene polymer, which has 70% or more of cis-1,4 bond and a molecular weight in the range of 10,000 to 150,000, in an amount of 0.3 to 12 mol% based on an isoprene monomer unit of the polymer is used as a low molecular weight diene polymer when the low molecular weight diene polymer is cyclized.

3. Detailed Description of the Invention

The present invention relates to a process for preparing cyclized polymer in which a low molecular weight isoprene polymer, which is modified by a compound having a specific functional group, is used as a starting material.

Natural rubbers (NR) and isoprene rubbers such as synthetic isoprene rubbers (IR) are easily cyclized by the presence of an acid catalyst and the cyclized rubber thus obtained has features such as excellent adhesiveness to polyolefine, adhesive property to metal, abrasion resistance, and chemical resistance. Therefore, it has been used for adhesive agents, coating compounds, vehicles for printing ink, electrical insulation

materials, and the like. Further, in recent years, its application to photosensitive materials has also been attempted from the point of view of having a highly reactive double bond in a molecular chain.

However, natural rubbers (NR) and synthetic isoprene rubbers (IR) that are conventionally used as starting materials of cyclized polymer are polymers with extremely high molecular weights and the dissolving activity is significantly inferior, and thus it is necessary to perform cyclization reaction at a low concentration. As a result, the productivity has been very low. Further, the cyclized rubber produced by reaction at a low solids concentration, disregarding the productivity, is not only inferior in compatibility with highly polar resins such as alkyd resins but also insufficient in adhesive property to polyolefine or metal.

In order to reduce these disadvantages, various use of a low molecular weight rubber has been proposed. However, the cyclized polymer obtained by using it does not satisfy the desires in terms of adhesive property and compatibility with resin.

The present inventors have dedicated themselves to the examination in order to easily prepare a cyclized polymer excellent in adhesive property and compatibility with resins. As a result, they have found out that a modified low molecular weight isoprene rubber produced by adding maleic anhydride or its derivative to a low molecular weight isoprene polymer, which has 70% or more of cis-1,4 bond and a molecular weight in the range of 10,000 to 150,000, in an amount of 0.3 to 12 mol% based

on an isoprene monomer unit of the polymer is used as a low molecular weight diene polymer when the low molecular weight diene polymer is cyclized to produce a cyclized polymer whose iodine number is 100 to 300, and thus a cyclized polymer excellent in adhesive property and compatibility, namely, suitable for printing ink, coating compounds, coating materials and the like can be obtained without losing the excellent performance that the cyclized polymer originally has. They have completed the present invention based on these findings.

In the preparation process of the present invention, firstly, it is important to use low molecular weight isoprene polymers having specific microstructures and molecular weights which are used as bases for modified polymers to be cyclized. That is, the low molecular weight isoprene polymer must have 70% or more of cis-1,4 bond and a molecular weight in the range of 10,000 to 150,000.

When the amount of cis-1,4 bond is lower than the above-mentioned range, the performance of a cyclized polymer to be finally obtained as a film is inferior. For example, in the case where the isoprene polymer is used as a coating compound or a printing ink, the coating film becomes brittle and is not suitable for practical use. Therefore, the amount of cis-1,4 bond is preferably 80% or more from such a viewpoint. In this regard, the amount of cis-1,4 bond is determined by infrared absorption spectrometry.

In addition, when the molecular weight is less than 10,000, the film physical properties of the cyclized polymer obtained

is poor. In the case where it is used as a coating compound, the coating film is easily deteriorated and becomes brittle. On the other hand, if the molecular weight exceeds 150,000, the solution viscosity of the cyclized polymer obtained is too high as it is dissolved in a solvent for use. Thus, the workability becomes significantly poor. The molecular weight is more preferably about 20,000 to 80,000 from such a viewpoint. Here, the term "molecular weight" as used herein means a viscosity average molecular weight (M_v) and it is calculated from the limiting viscosity ($[\eta]$) in a toluene solution at 30°C using the following equation.

$$[\eta] = 1.21 \times 10^{-4} M_v^{0.77}$$

Examples of such low molecular weight isoprene polymers having specific microstructures and molecular weights include a low molecular weight isoprene polymer obtained by anionic polymerization method and a low molecular weight isoprene rubber of an oxidative degradation form which is obtained by thermal decomposition of a solid rubber such as natural rubber (NR) or a high molecular weight synthetic isoprene rubber (IR) which is produced by using Ziegler catalyst or lithium catalyst. However, the quality of the low molecular weight isoprene polymer of an oxidative degradation form is unstable and further the isoprene polymer contains a large amount of impurities. Therefore, it is preferable to use the low molecular weight isoprene polymer which is obtained by anionic polymerization method.

As described above, the low molecular weight isoprene

rubber produced by anionic polymerization method can be obtained by polymerizing isoprene monomer, or isoprene monomer and monomer, for example, a small amount of butadiene and styrene which may be copolymerized with isoprene using a lithium polymerization catalyst in the presence or absence of a polymerization catalyst. Typical examples of the lithium polymerization catalyst include metallic lithium or organolithium such as methyl lithium, propyl lithium, butyl lithium, α -naphthyl lithium, methylene dilithium, distyrenyl lithium. As well known, the molecular weight of the low molecular weight isoprene polymer is easily controlled by the use ratio of the isoprene monomer to the catalyst. Additionally, the polymerization is easily controlled when the polymerization catalyst is used, and thus it is appropriate to use it. Examples thereof include inert hydrocarbons such as n-butane, isopentane, n-hexane, n-heptane, benzene, and xylene. It should be noted that if a polar hydrocarbon compound is present in a polymerization system, the amount of cis-1,4 bond of the polymer to be obtained may often be lower.

Maleic anhydride, maleic acid, maleate, maleic acid amide, or maleic anhydride derivative such as maleimide is added to such low molecular weight isoprene polymers having specific microstructures and molecular weights to produce a modified low molecular weight isoprene polymer, which is used as a starting material of cyclized polymer. Addition reaction of maleic anhydride or its derivative to the low molecular weight isoprene polymer is easily proceeded, for example, by adding maleic anhydride or its derivative to the low molecular weight isoprene

polymer and heating and reacting in the presence or absence of a solvent or a radical catalyst. Examples of the catalyst to be used herein include n-butane, n-hexane, n-heptane, cyclohexane, benzene, toluene, xylene, and halide thereof such as halogenated hydrocarbon. In addition to the modified low molecular weight isoprene polymer as described above, examples of the modified low molecular weight isoprene polymer to be used in the present invention include: a modified low molecular weight isoprene polymer in which one or both carboxyl groups based on maleic anhydride are esterified by reacting the maleic anhydride group which is added and introduced into a low molecular weight isoprene polymer with alcohols such as methanol, ethanol, and propanol, for example, in the presence or absence of a catalyst such as p-toluenesulfonic acid; a modified low molecular weight isoprene polymer which is amidated by reaction with primary monoamines such as ammonia, propyl amine, butylamine; a modified low molecular weight isoprene polymer which is imidized by dehydration reaction of the amidated product above; a modified low molecular weight isoprene polymer which is amidated by reaction with amino alcohols such as ethanolamine and isopropanolamine and further dehydrated to form N-(aminohydrocarbyl)maleimide; and a modified low molecular weight isoprene polymer which is amidated by reaction with a primary/tertiary diamine and dehydrated to form N-(hydroxyhydrocarbyl)maleimide. Such derivatization reactions are performed after the addition of maleic anhydride to the low molecular weight isoprene polymer.

Among these modified low molecular weight isoprene polymers, the modified low molecular weight isoprene polymer in which a maleic anhydride group of the modified low molecular weight isoprene polymer has the form of an alcoholic derivative, a derivative of amines, and a derivative of imides is preferable rather than the modified isoprene polymer to which maleic anhydride is added, from a point of view of the viscosity stability over a long period of time in itself.

Thus, in the preparation process of the present invention, the modified low molecular weight isoprene polymer, i.e., a starting material of cyclized polymer, is produced. Here, it is important that the amount of maleic anhydride or its derivative (hereinafter referred to as addition amount) which is added to the low molecular weight isoprene polymer should be 0.3 to 12 mol% based on an isoprene monomer unit of the polymer. When the addition amount is too low, an effect on the adhesive property and compatibility with resin of a cyclized polymer to be finally obtained is not much improved. On the other hand, when the addition amount is too high, the solution viscosity is too high as it is dissolved in a solution. Thus, the workability becomes significantly poor. Therefore, a desired purpose cannot be achieved. Based on this standpoint, a more preferable addition amount is 1 to 6 mol%.

Conventionally known methods can be used as the method for cyclizing the modified low molecular weight isoprene polymer. For example, the cyclized polymer can be prepared by a process involving the steps of: dissolving the modified low molecular

weight isoprene polymer in solvent of aromatic hydrocarbons such as benzene, toluene, and xylene; adding organic sulfonic acids such as concentrated sulfuric acid or P-toluenesulfonic acid; Friedel crafts catalysts such as tin tetrachloride and titanium tetrachloride; hydrogen halides such as hydrogen chloride and hydrogen bromide; nonmetallic halide such as boron trichloride; or phosphorus compounds such as phosphorus pentaoxide and phosphoryl trichloride; and heating the mixture. Alternatively, the cyclized polymer can be prepared by a process involving the steps of: dispersing the modified low molecular weight isoprene rubber polymer in water in the presence or absence of a surfactant to produce an aqueous dispersing element; adding the above-mentioned catalyst; and heating and reacting. Further, it can be obtained by directly placing it in a roll mill and then heating and mixing with catalysts. In the cyclization reaction, a mixture of natural rubber (NR) and synthetic isoprene rubber (IR) may be used with an amount not departing from the spirit of the invention. When the reaction is performed in a solution, the concentration of the modified low molecular weight isoprene rubber polymer may be about 5 to 80%. In any of methods, the reaction is carried out at room temperature to 200°C, preferably at 80 to 150°C for 2 to 10 hours.

The cyclization reaction is carried out with the reaction temperature, reaction time, and concentration of reaction system determined so that the iodine number of the cyclized polymer is in the range of 100 to 300. When the iodine number is smaller than 100, the cyclized polymer to be produced becomes brittle.

As a result, it is difficult to apply it to the application of coating materials, printing ink, or the like. On the other hand, when the iodine number is larger than 300, the adhesive property and close adhesion of the cyclized polymer to be produced are insufficient, which is not desirable. Based on this standpoint, the iodine number is more preferably in the range of 170 to 280.

Needless to say, the cyclized polymer to be obtained by the process of the present invention originally has characteristics such as abrasion resistance and chemical resistance, and further has characteristics of improved adhesive property, adhesion to polyolefine and the like, compatibility with alkyd resins or polar resins.

If necessary, various compounding agents are added to such a cyclized polymer, which is preferably used as a printing ink, a coating material for polyolefine, a coating material for waterproof and corrosionproof, a coating agent, a wetting-out agent for waterproofing concrete, a chemical-resistant coating agent, an electric insulation material, an adhesive agent for materials such as rubber and metal, a photopolymer material such as photoresist, or a compounding agent to improve the hardness of rubber and modulus. Furthermore, it may be used as a compounding agent in order to improve the adhesive property and compatibility of the cyclized polymer (cyclized rubber) obtained from natural rubber (NR), synthetic isoprene rubber (IR), and the like.

Herein below, the present invention will be specifically described with reference to Examples, but it is not to be construed

as being limited thereto.

Example 1

Isoprene monomer was placed in a pressure polymerization vessel using n-heptane as a solvent and then n-butyl lithium was added as a catalyst, which was polymerized in an inert gas atmosphere at 60°C for 5 hours. After the end of polymerization, a polymerized solution was washed and dried under reduced pressure. A viscous solution of a low molecular weight isoprene polymer was obtained. With reference to the polymer, the amount of cis-1,4 bond and the viscosity average molecular weight were evaluated by infrared absorption spectrometry and viscosity method. As a result, the amount of cis-1,4 bond was 83% and the viscosity average molecular weight was 31,000. After dissolving the low molecular weight isoprene polymer in toluene, maleic anhydride was added in an amount of 0.4 to 20 parts by weight based on 100 parts by weight of the polymer, which was stirred at 180°C and a modified low molecular weight isoprene polymer to which maleic anhydride was added in an amount of 0.27 to 13.2 mol% based on an isoprene monomer of the low molecular weight isoprene polymer was obtained.

100 parts by weight of the modified low molecular weight isoprene polymer was dissolved in 100 parts by weight of toluene and 5 parts by weight of P-toluenesulfonic acid was added as a catalyst, which was stirred at 100°C and then subjected to cyclization reaction. After the end of reaction, the reaction solution was cooled and 4 parts by weight of aqueous ammonia

(25% concentration) was added to stop the reaction. Then, the reaction solution was washed, followed by pouring into methanol, fractionating cyclized polymer, and drying.

The cyclized polymer obtained was a yellow-brown solid. The iodine number was evaluated by the Wijs method and the results are shown in Table 1. Cyclization reaction was performed using an unmodified low molecular weight isoprene polymer in place of the modified low molecular weight isoprene polymer and a yellow-brown cyclized polymer with an iodine number of 209 was obtained.

20 parts by weight of the cyclized polymer thus obtained was respectively dissolved in 100 parts by weight of toluene and 20 parts by weight of titanium oxide was added thereto to prepare a so-called ink composition. The composition was applied onto a low density polyethylene film having 0.2 mm thickness using a barcoater and dried at room temperature overnight. Subsequently, the coating film obtained was subjected to the adhesive tape peeling test. Adhesive tape was applied on the coating film and then the tape was stripped to observe any peeling of the coating film. In this way, the adhesion of the ink composition containing cyclized polymer to the polyethylene film was evaluated. The results are illustrated in Table 1. In the case where the peeling was not observed at all, the result was indicated by "excellent". When the peeling was observed in a small part of the film at the rate of once per about ten times, the result was indicated by "Fair". Further, when the peeling was observed in a part of the film

each time, the result was indicated by "improper".

Further, the polyethylene film to which the ink composition was applied in the same manner as described above was crumpled by hands about 20 times and then the change in the surface of the coating film was observed (hereinafter referred to as crumple test). Then, the cracked surface of the coating film by crumpling was evaluated. The results are illustrated in Table 1. In the case where the crack was not observed at all, the result was indicated by "excellent". When the crack was observed occasionally, the result was indicated by "Fair". When many cracks were observed, the result was indicated by "improper".

Further, 10 parts by weight of cyclized polymer and 10 parts by weight of alkyd resin (trade name: Phthalkid (transliteration) 355-50, manufactured by Hitachi Chemical Co., Ltd.) were dissolved in 100 parts by weight of toluene. The solution was casted on a glass slide and then dried. The condition of the obtained layer was observed and the compatibility of the cyclized polymer to the alkyd resin was examined (hereinafter referred to as compatibility test). The results are illustrated in Table 1. In the case where a uniform and transparent layer was formed, the result was indicated by "excellent". When an acceptable transparent layer (not fully satisfactory, but has transparency) was formed, the result was indicated by "Fair". When an opaque and phase separated layer was formed, the result was indicated by "improper". In the case where the modified low molecular weight isoprene polymer to which maleic anhydride was added in an amount of 11.9 and 12.5 mol%

was used, the dissolving activity was significantly poor.

Table 1

	1	2	3	4	5	6	7	8
Addition amount of MAn of modified PIP (mol%)	0	0.27	0.33	1.1	3.3	5.9	11.9	12.5
Iodine number of cyclized polymer (Wijs method)	209	211	211	212	215	217	220	220
Results of adhesive tape peeling test	Improper	Fair	Good	Excellent	Excellent	Excellent	Excellent	Excellent
Results of crumple test	Improper	Improper	Good	Excellent	Excellent	Excellent	Excellent	Excellent
Results of compatibility test	Improper	Fair	Excellent	Excellent	Excellent	Excellent	Fair	Improper

Example 2

A modified low molecular weight isoprene polymer whose additive amount of maleic anhydride was 1.3 mol% was obtained in the same manner as described in Example 1 except that the additive amount of maleic anhydride was 2 parts by weight.

100 parts by weight of the modified low molecular weight isoprene polymer was dissolved in 50 parts by weight of toluene and 5 parts by weight of concentrated sulfuric acid (98%) and 5 parts by weight of titanium tetrachloride were added as catalysts, which was stirred at 100°C and then subjected to cyclization reaction. After the end of reaction, cyclized polymer was fractionated and dried in the same manner as described in Example 1.

The obtained cyclized polymer was a yellow-brown solid

and its iodine number was 201.

This cyclized polymer was subjected to the adhesive tape peeling test, the crumple test, and the compatibility test in the same manner as described in Example 1 and the performances such as the adhesive property and compatibility were examined. The results are illustrated in Table 2. The cyclized polymer exhibited excellent performances in each test.

Example 3

A low molecular weight isoprene polymer having 85% of cis-1,4 bond and a viscosity average molecular weight of 58,000 was obtained in the same manner as described in Example 1 except that the amount of n-butyllithium used was changed. This polymer was reacted with maleic anhydride in the same manner as described in Example 1 and a maleic anhydride-modified low molecular weight isoprene polymer whose additive amount of maleic anhydride was 2.4 mol% was produced. Then, the maleic anhydride modified isoprene polymer was contacted with methanol at 70°C and a modified low molecular weight isoprene polymer to which maleic acid monomethyl ester was added was obtained.

100 parts by weight of this modified polymer was dissolved in 100 parts by weight of toluene and 10 parts by weight of P-toluenesulfonic acid was added as a catalyst, which was reacted at 100°C under stirring and 10 parts by weight of aqueous ammonia was added to stop the reaction. Then, the reaction solution was washed, followed by pouring into methanol, fractionating cyclized polymer, and drying.

The cyclized polymer thus obtained was a yellow solid and its iodine number was 238.

This cyclized polymer was subjected to the adhesive tape peeling test, the crumple test, and the compatibility test in the same manner as described in Example 1 and the performance was examined. The results are illustrated in Table 2. The cyclized polymer was excellent in adhesive property and compatibility.

Example 4

Dimethylaminopropyl amine was added to the modified low molecular weight isoprene polymer to which maleic acid was added, which was used in Example 1, and the added maleic anhydride group was semi-amidated. Furthermore, the semi-amidated product was heated at 150°C and a modified low molecular weight isoprene polymer to which N-(dimethylaminopropyl)-maleimide was added was given.

Cyclization reaction was performed in the same manner as described in Example 1 using the modified polymer and a yellow-brown cyclized polymer with an iodine number of 227 was obtained.

This cyclized polymer was subjected to the adhesive tape peeling test, the crumple test, and the compatibility test in the same manner as described in Example 1 and the performance was examined. The results are illustrated in Table 2. The cyclized polymer was excellent in adhesive property and compatibility.

Table 2

(Preparation) Examples of the used cyclized polymers	Example 2	Example 3	Example 4
Results of adhesive tape peeling test	Excellent	Excellent	Excellent
Results of crumple test	Excellent	Excellent	Excellent
Results of compatibility test	Excellent	Excellent	Excellent

As is apparent from Table 1, each of the cyclized polymers obtained in Examples 2 to 4 was excellent in adhesive properties and compatibility with resin. However, the cyclized polymer in Comparative example 1 was insufficient in adhesive properties and also inferior in compatibility.

6. Contents of the amendment

(1) The description "the performance of a cyclized polymer to be finally obtained as a film is inferior" (the specification, page 4, lines 19 to 21) is corrected to "when a cyclized polymer to be finally obtained is used to form a film, physical properties of the film are inferior".

(2) The term "such derivatization reactions" (the specification, page 8, lines 2 and 3) is corrected to "reactions for producing such derivatives".

(3) The term "the low molecular weight isoprene polymer" (the specification, page 11, line 20) is corrected to "the low molecular weight isoprene polymer (abbreviated as PIP in Table 1)".

(4) The term "maleic anhydride" (the specification, page

11, line 21) is corrected to "maleic anhydride (abbreviated as MAn in Table 1)".

(5) The description in Table 1 (the specification, page 14) is corrected as follows:

Table 1

	Comparative Example		Example					Comparative Example
Experiment No.	1	2	3	4	5	6	7	8
Addition amount of MAn of modified PIP (mol%)	0	0.27	0.33	1.1	3.3	5.9	11.9	12.5
Iodine number of cyclized polymer (Wijs method)	209	211	211	212	215	217	220	220
Results of adhesive tape peeling test	Improper	Fair	Fair	Excellent	Excellent	Excellent	Excellent	Excellent
Results of crumple test	Improper	Improper	Fair	Excellent	Excellent	Excellent	Excellent	Excellent
Results of compatibility test	Improper	Fair	Excellent	Excellent	Excellent	Excellent	Fair	Improper

Modified PIP is a modified low molecular weight polymer which is obtained by adding maleic anhydride to a low molecular weight isoprenepolymer having 83% of cis-1,4 bond and a viscosity average molecular weight of 31,000. MAn is maleic anhydride.

(6) The description "used in Example 1" (page 16, line 19) is corrected to "used in Experiment 4 of Example 1".

(7) The description "as is apparent from Table 1, each of the cyclized polymers obtained in Examples 2 to 4 was excellent in adhesive properties and compatibility with resin. However, the cyclized polymer in Comparative example 1 was insufficient

in adhesive properties and also inferior in compatibility" indicated below Table 2 of page 17 is corrected to "as is apparent from Table 2, each of the cyclized polymers obtained in Examples 2 to 4 was excellent in adhesive properties and compatibility with resin".